Technical University of Denmark

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Maresca, Alberto; Astrup, Thomas Fruergaard

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COLUMN LEACHING FROM BIOMASS COMBUSTION ASHES

A. MARESCA*, T.F. ASTRUP*

** Department of Environmental Engineering, Technical University of Denmark, building 113, DK-2800 Kgs. Lyngby, Denmark*

SUMMARY: The utilization of biomass combustion ashes for forest soil liming and fertilizing has been addressed in literature. Though, a deep understanding of the ash chemical composition and leaching behavior is necessary to predict potential benefits and environmental risks related to this practice. In this study, a fly ash sample from an operating Danish power plant based on wood biomass was collected, chemically characterized and investigated for its leaching release of nutrients and heavy metals. A column leaching test was employed. The strongly alkaline pH of all the collected eluates suggested the potential suitability of the ash as a liming material. Although high contents of nutrients were detected, differences in their leaching release were found. Heavy metals were detected within typical literature contents for Nordic countries ashes.

1. INTRODUCTION

Consumption of sustainable energy sources has been notably increasing in Denmark (Danish Energy Agency, 2012), in line with the European Directive 2009/28/EC for renewable energy use. In this framework, increasing amounts of biomass (e.g. wood and straw) have been combusted for energetic purposes. Indicatively, consumption of wood chips for primary energy production has increased of about four times in the period 2000-2012 (Danish Energy Agency, 2012). From a global warming perspective, the process can be considered sustainable as long as new biomass is planted, since the CO_2 released in the combustion process is taken up during the growth of new plants. Burning wood produces about 2% by weight of ash (James et al., 2012). The management of these ash residues is typically country specific; generally, if not differently regulated, landfill is the solution.

Several studies have demonstrated the alkaline nature of wood ashes and utilization options as a potential liming material for forest soils have been reported (e.g. Barbosa et al., 2013; Stig and Swedish Forest Agency, 2006). Additionally, wood ash generally contains considerable amounts of nutrients which would benefit the soil fertility (e.g. Ingerslev et al. 2011; Olanders & Steenari 1995). Therefore, a few countries in Europe (e.g. Denmark, Sweden, Finland and Austria) have regulated the applicable doses of ashes on land depending on compositional data. Guidelines can also be found (Hjerpe and Swedish Forest Agency, 2008; Stupak et al., 2008).

Despite the use of ash on forest soils could both counteract acidification and provide valuable nutrients, environmental risks may be associated with this practice. Precisely, contamination risks may derive from the potential contents of heavy metals (e.g. As, Cr, Cd, Ni and Pb) and organic compounds (e.g. PAHs), which thus need to be taken into account (e.g. Li et al. 2012;

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Straka & Havelcová 2012; Karltun et al. 2008).

Furthermore, availability of the different compounds will be affected by the mineralogy and the composition of the ashes. On one hand, the chemical composition, as well as the physical properties and the mineralogy, could significantly vary from ash to ash depending on the origin of the fuel, the combustion technology, the ash type (i.e. bottom ash or fly ash) and the power plant's operating parameters (Etitgni and Campbell, 1991; Someshwar et al., 1990). Moreover, depending on the ash mineralogy and composition, some compounds may be easily soluble (e.g. salts) and leach out rapidly, while others may be strongly bound to the ash matrix and take longer times before actually being released.

Leaching tests have provided thorough information about release of ash constituents and their potential for an environmental contamination. Several standard leaching methods are in fact available to characterize the leaching properties of waste materials. During this study, a fly ash sample from a Danish biomass combustion plant was collected and a column leaching test was employed to investigate the release of a few selected elements over increasing liquid to solid (L/S) ratios. The leaching of nutrients (i.e. K and P) as well as heavy metals (i.e. Cr and Pb) has been investigated in comparison with the respective contents in the ash. The study represents preliminary results as the research is still ongoing.

2. MATERIALS AND METHODS

2.1 Sampling and chemical characterization

Fly ash residues from a Danish biomass combustion plant burning wood chips, mainly from *Picea abies*, were sampled late January 2014. The material was firstly dried at 110 °C and then milled by means of a vibrating disc mill (agate discs) in order to reduce the sample grain size. A subsample of 0.25 g was digested by microwave assisted digestion (Multiwave Anton Paar 3000), using 6 ml of HNO_3 (65%), 2 ml of HCl (37%) and 2 ml of HF (40%), according to EN 13656: 2003. In order to support the oxidation of the organic matter, 2 ml of H_2O_2 (30%) were additionally added; here, 12 ml of H_3BO_3 (10%) were used to complex with HF. Duplicates, blanks and a certified reference material (BCR-176R) were also digested to validate the results. The digested samples were then analyzed by ICP-MS (7700x, Agilent Technologies) for the contents of Cr, P and Pb, and by ICP-OES (Varian Vista-MPX) for the contents of K and Ca.

2.2 Leaching test

A standard column leaching test was carried out according to CEN/TS 14405: 2004 using untreated ash. A 30 cm height plexiglass column (ø: 5 cm) was established. A thin layer of acid-washed sand and a nylon filter (PA 6.6 - mesh opening: 20 µm) were additionally included at the very top and bottom of the column. Distilled water was pumped into the system at a constant flow rate of 12 ml/h. For the first three days, the leachate was recirculated to ensure initial equilibrium conditions. Thereafter, the exiting leachate was regularly sampled, filtered through a 0.45 µm PTFE Hydrophilic filter, acidified with HNO_3 and eventually analyzed by means of ICP-MS/OES for the concentration of K, P, Cr and Pb. The leaching test was stopped at the L/S ratio of 20 l/kg.

2. RESULTS AND DISCUSSION

This study investigated the content and release of a few selected nutrients, heavy metals and major elements from biomass combustion ashes. Table 1 summarizes the analytical results for the contents of K, P, Pb, Cr and Ca in comparison with literature for typical Nordic countries fly ashes (Morten Ingerslev et al., 2011; SLU, 2008) and the Danish limit values for utilization of biomass combustion ash on top of forest soils. Although the content of K was found to be slightly lower than in the presented literature, all the other elements were detected within typical variation ranges. In agreement with previous studies (e.g. Demeyer et al., 2001; Ingerslev et al., 2011; Kilpimaa et al., 2013; Olanders and Steenari, 1995) high contents of nutrients and low contents of heavy metals were detected. High contents of Ca were also measured.

The solely content of nutrients, as well as heavy metals, cannot predict their release or availability. Therefore, a standard column test was employed. Electrical conductivity and pH were measured in all the collected samples and Figure. 1 shows the analytical results. A pH of 13.5 was measured at the beginning of the experiment; then it slowly decreased and eventually levelled off at the pH of 13. The electrical conductivity showed a rapid drop from 90 mS/cm to 8 mS/cm before the L/S of 5 l/kg, likely because of the initial wash out of easily soluble salts, and then levelled off until the end of the experiment (see Figure. 1).

A rather fast release of K was detected at the beginning of the experiment, where a drop of about two orders of magnitude was measured in the eluates concentration (Figure. 2a). Nevertheless, relatively high concentrations of K were measured also at the end of the experiment, namely at 42.000 µg/l. Differently, only marginal amounts of P were leached (Figure. 2b), suggesting differences in the release mechanisms and availabilities of the two nutrients in agreement with previous studies (e.g. Röser et al., 2008; Steenari and Lindqvist, 1997). Relatively small amounts of Cr and Pb were released by the end of the leaching test and, while Pb seemed to reach a rather stable concentration towards the end of the experiment, Cr showed a decreasing behavior (Figure 2c and 2d).

When ashes are spread on forest soil, local conditions (e.g. rain, soil pH and temperature) would significantly differ from a standard leaching test as the one described above. Therefore, the release of the different compounds will not necessarily follow the trends shown in the results. Nevertheless, we expect a rather fast release of salts at the beginning of the ash application, as shown in Figure 1b and Figure 2a by the rapid drop in the electrical conductivity and the K concentration. Similar findings have been reported in literature, often in relation to field studies, by Augusto et al., (2008), Jacobson et al. (2014), Karltun et al. (2008), Samuelsson and National Bord of Forestry (2002).

Wood ashes can be employed for liming purposes because of their contents of Ca and Mg carbonates (e.g. Pitman, 2006). Strongly alkaline pH values were measured in all the eluates, as an indication of the potential long term dissolution of hydroxides and oxides (Karltun et al., 2008). High contents of Ca were also detected in the investigated ash sample.

Overall, the results suggest that biomass combustion ashes are potentially suitable for liming purposes, although a more detailed investigation would be necessary to confirm the long term liming effect of the wood ash sample. However, further studies are needed to investigate the release of other nutrients, especially if the ashes are meant to be used as a soil conditioner. Although Cr and Pb were detected in contents comparable to literature and below Danish limit values for application onto soil (BEK 818:, 2008), further investigations in a view of a potential contamination of the environment by other pollutants should be carried out.

5. CONCLUSIONS

A wood ash sample from biomass combustion has been tested for contents and leaching of nutrients and heavy metals. To the extent of the investigated elements, the sample showed contents of nutrient and heavy metals in line with literature.

Table 1. Contents of K, P, Cr, Pb and Ca in the wood ash sample measured by means of ICP-MS/OES in comparison with BEK 818: 2008, Ingerslev et al. (2011) and SLU (2008). The values are expressed in mg/kg TS^{-1}. *SLU (2008): selected parameters: burner_ grate boiler; ash type_ fly ash; fuel type_ wood. Minimum and maximum values represent the 95% confidence interval.

Element	**This study**	**SLU (2008)***	**Ingerslev et al. (2011)**	**BEK 818: 2008**
K	39.000	63.000 – 85.000	44.000	
P	22.000	14.000 – 18.000	17.000	
Cr	60	54 – 67	160	100
Pb	53	140 -190	20	250
Ca	190.000	220.000-280.000	130.000	

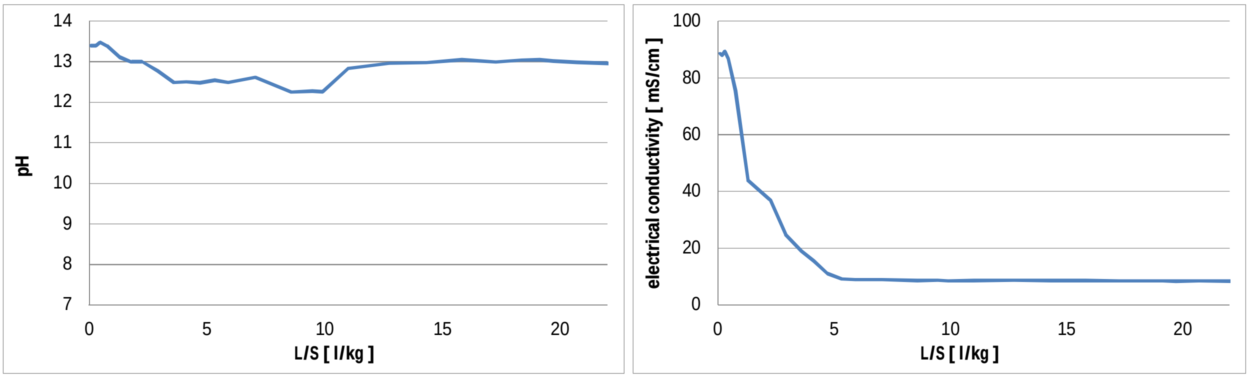

Figure.1. Trend of pH (on the left) and electrical conductivity (on the right) against the L/S ratio

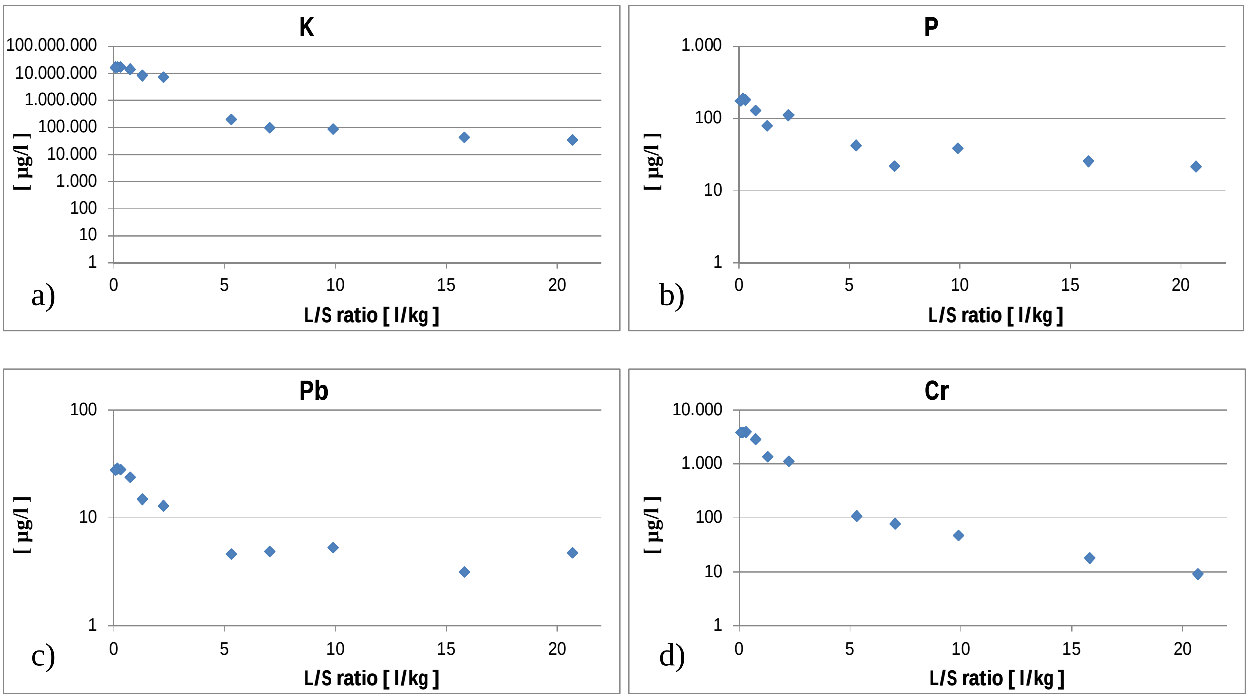

Figure. 2. Concentrations of K (a), P (b), Pb (c) and Cr (d) in the eluate samples. Concentration values measured by means of ICP-MS / OES. The presented values are expressed in µg/l

Although similar contents of K and P were detected in the ashes, their release was significantly different, likely due to differences in the mineralogical composition and release mechanisms. The strongly alkaline pH values measured in all the eluates samples suggested the potential suitability of the ash for liming purposes. The results of this study are preliminary and limited only to a few elements. To assess the benefits and risks associated to ash utilization, a broader share of compounds should be taken into account.

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